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“Burst-like” Characteristics of the β/β' Phase Transformation in Pu-Ga Alloys

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ABSTRACT

The β to β' phase transformation in Pu-Ga alloys is intriguing for both scientific and technological reasons. On cooling, the ductile fcc β -phase transforms martensitically to the brittle monoclinic β' -phase at approximately -120°C (depending on composition). This exothermic transformation involves a 20% volume contraction and a significant increase in resistivity. The reversion of β' to β involves a large temperature hysteresis beginning just above room temperature. In an attempt to better understand the underlying thermodynamics and kinetics responsible for these unusual features, we examined the β/β' transformations in a 0.6 wt% Pu-Ga alloy using differential scanning calorimetry (DSC) and resistometry. Both techniques indicate that the martensite start temperature is -120°C and the austenite start temperature is 35°C . The heat of transformation is approximately 3 kJ/mole. During the $\beta' \rightarrow \beta$ reversion, “spikes” and “steps” are observed in DSC and resistometry scans, respectively. These spikes and steps are periodic, and their periodicity with respect to temperature does not vary with heating rate. With an appropriate annealing cycle, including a “rest” at room temperature, these spikes and steps can be reproduced through many thermal cycles of a single sample.

INTRODUCTION

Although plutonium and its alloys have been utilized for over fifty years, we still do not have a thorough understanding of their underlying materials science. In particular, pure Pu exists in 6 solid phases, and the transformations between the phases are not fully understood. In pure Pu, the β phase (monoclinic) is stable at ambient conditions, but small additions of an alloying element such as Ga can cause the higher temperature β phase (fcc) to be retained at room temperature for hundreds or thousands of years [1]. At subambient temperatures, the β phase transforms to a metastable mixture of β and β' (β' is a monoclinic phase with Ga supersaturated in the lattice). The transformation has a sizeable hysteresis, and the β' does not revert back to β until it is heated above ambient temperatures. According to the equilibrium phase diagram [1,2], a mixture of $\beta + \text{Pu}_3\text{Ga}$ is stable at ambient conditions, but we do not fully understand how or when the transformation from metastable $\beta' + \beta$ to stable $\beta + \text{Pu}_3\text{Ga}$ occurs.

Using a combination of experimental and modeling techniques we are investigating the thermodynamics and kinetics of the $\beta \leftrightarrow \beta'$ phase transformations in a Pu-0.6 wt% Ga alloy. Based on TTT curves published by Orme and Faires [3], we expect that the maximum amount of transformation to β' in this alloy is $\sim 30\%$. Because the resistivities of the β' and β phases differ by 45% at room temperature, resistometry provides excellent sensitivity for monitoring the progress of the transformations. We are also using differential scanning calorimetry (DSC) to determine transformation temperatures and heats of transformation. The densities of β' and β differ by 20%, which indicates that elastic and plastic work must be involved in the transformation. Finite element models are used to calculate the amount of work involved in the transformation and to predict the hysteresis.

Here, we report two particularly interesting phenomena observed during thermal cycling experiments of a Pu-0.6 wt% Ga alloy. First, we show evidence for a burst-like transformation during the $\beta' \rightarrow \beta$ reversion on heating. DSC, resistometry, and dilatometry [4] all indicate that the transformation occurs in a “burst-like” progression as the temperature is increased. We analyze this data in terms of a simple thermodynamic model. Second, we describe an unexpected room temperature “annealing” requirement for reproducible transformation in a Pu-Ga

sample. A sample can be thermally cycled many times, but it must be “annealed” at room temperature *after* a high temperature anneal to obtain reproducible results.

EXPERIMENTAL

We investigated a Pu-0.6 wt% Ga alloy using (DSC) and resistometry. This alloy was prepared by induction heating and was approximately two years old. Resistometry data was obtained with a four-point probe using discs with a diameter of 2.8 mm and a thickness of 0.1 mm. The four probes were 0.01” diameter copper wires which ran across the samples. Samples were kept under vacuum (typically 10^{-5} torr) and could be thermally cycled between 20 K and 700 K using a flow through helium cryostat. Heating rates as high as 5°C/min were achieved, although most data was obtained during cycles at 1.5°C/min.

A Perkin-Elmer Diamond DSC equipped with a liquid nitrogen cooling system was used to thermally cycle samples between –160°C and 350°C. The pans were gold-plated stainless steel with a threaded lid that sealed against a gold-plated copper gasket, and were rated to withstand 150 atm at 400°C. Although these pans are massive compared to the Al or Cu pans typically used for DSC experiments, they were chosen to provide sufficient containment. The purge gas used was a mixture of 90%Ne and 10%He. This mixture can be used from –176°C to 585°C, so problematic gas switching during thermal cycles was unnecessary [5].

RESULTS AND DISCUSSION

Transformation temperatures and heats of transformation

Using resistometry and DSC, martensite start (M_S) and austenite start (A_S) temperatures of –120°C and 35°C, respectively, were measured. The data from the two techniques were in excellent agreement and the scans were reproducible within a few degrees. Figure 1 shows resistometry data for seven thermal cycles at 1.5°C/min. Each cycle had the following sequence: 25°C → –200°C → 350°C → 25°C. The marked increase in resistivity at ~–120°C signals the beginning of β' phase formation. Likewise, the decrease in resistivity beginning around 35°C corresponds to reversion to the β phase. In the DSC, the cycle was similar, except the lower limit was –160°C. Figures 2a and 2b show the cooling and heating portions of a single DSC thermal cycle at 20°C/min. The $\beta \rightarrow \beta'$ transformation is marked by an exothermic peak with an onset of –121°C; the $\beta' \rightarrow \beta$ reversion is an endotherm with an onset of 31°C. Figure 2b also shows an additional endotherm corresponding to $\beta \rightarrow \beta$ transformation. Prior to the first DSC experiment, the sample was annealed into the $\beta + \beta$ phase field where Ga rapidly diffuses out of the β phase. Upon cooling, the Ga-lean regions transform to the β , β and β phases, and these transformations ultimately result in pre-existing β phase remaining at room temperature. After several thermal cycles, this peak disappeared.

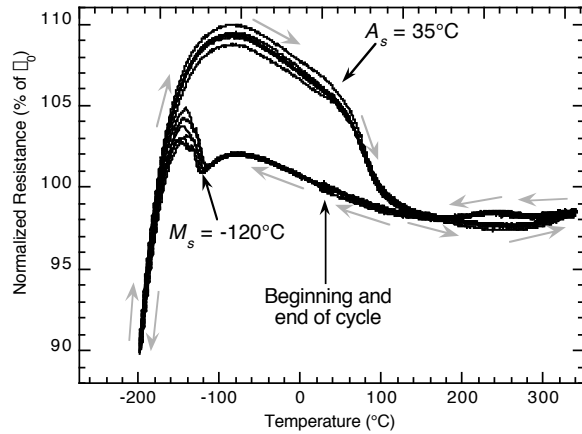


Figure 1. Resistometry data from thermal cycles at 1.5°C/min. The martensite start (M_s) temperature is -120°C and the austenite start temperature (A_s) is 35°C.

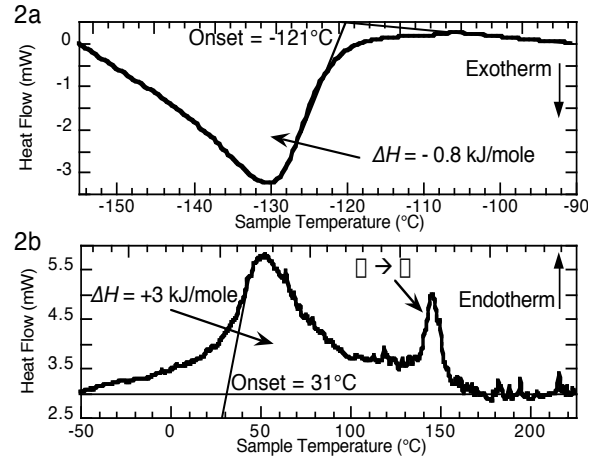


Figure 2. Cooling (a) and heating (b) portions of a DSC scan at 20°C/min. The exothermic $\square \rightarrow \square'$ transformation has an onset of -121°C and $\Delta H = -0.8$ kJ/mole. The onset of the $\square' \rightarrow \square$ reversion is 31°C and $\Delta H = +3$ kJ/mole.

Using resistivity data from the literature, we calculated the amount of transformation to the \square' phase, and then estimated the heats of transformation from the DSC data. Resistivity data for \square' was not available, so we used data for \square and extrapolated it to higher temperatures [6]. For the \square phase, data for a Pu-1.7 at% Ga (0.5 wt%) alloy were extrapolated to low temperatures [7]. From this data, we estimated that the maximum amount of transformation to the \square' phase was 25%. Thus, the areas of the DSC peaks (Figures 2a and 2b) correspond to only 25% of the total heat of transformation for each reaction. Total heats of transformation (ΔH_t) were estimated to be -0.77 kJ/mole for $\square \rightarrow \square'$ and 3 kJ/mole for $\square' \rightarrow \square$. The measured value of $\Delta H_t(\square \rightarrow \square')$ was believed to be a lower bound, because it is unlikely that the $\square \rightarrow \square'$ transformation proceeded to completion on cooling within the temperature range of the DSC peak. Furthermore, this additional transformation on heating was observed in our resistometry cycles and by other authors [8]. In the DSC, however, additional transformation may have been too slow to be discriminated from the baseline. Even though we measured values of $\Delta H_t(\square \rightarrow \square')$ far from the equilibrium temperature (T_0), we still expected the absolute values of $\Delta H_t(\square \rightarrow \square')$ and $\Delta H_t(\square' \rightarrow \square)$ to be equal. We therefore suggest that $\Delta H_t(\square \rightarrow \square')$ lies closer to -3 kJ/mole because the transformation volume and the DSC peak area are better defined for the reverse transformation. Because the observed heat flow included a contribution from the storage and release of elastic energy during the transformation and because finite-element modeling suggested that less elastic energy is released during \square' reversion than during \square' formation [9], $\Delta H_t(\square \rightarrow \square')$ was actually expected to be somewhat greater than $\Delta H_t(\square' \rightarrow \square)$. This difference, however, was not expected to be large.

Burst transformation

A series of “spikes” and “steps” corresponding to the $\square' \rightarrow \square$ reversion were seen in DSC and resistometry thermal cycles, respectively. In both cases, the spikes or steps became more pronounced as the heating rate decreased. This is particularly evident in Figure 3 which shows DSC traces at four heating rates ranging from 1.5°C/min to 20°C/min. In these scans, the “spikes” appear to be superimposed on a broad endothermic peak. Similar “spikes” have been observed in DSC scans of Pu-Ga alloys by other groups [4,10]. Close inspection of resistometry data between ~25°C and 125°C also reveals a series of “steps.” In differentiated resistometry data, the peaks in this region look distinctly different from the data surrounding this temperature range. Dilatometry data for a Pu-0.6 wt% Ga alloy published by Mitchell also shows a series of “steps” attributed to the $\square' \rightarrow \square$ reversion [4]. These “spikes” and “steps” observed by DSC,

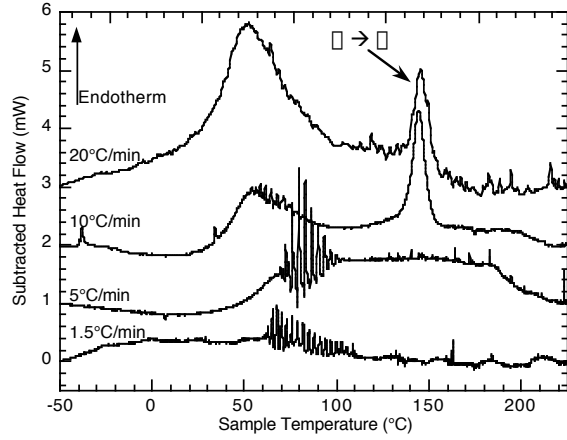


Figure 3: DSC heating scans at 1.5, 5, 10, and 20°C/min. Scans were offset along the y-axis for clarity. Distinct “spikes” corresponding to the $\square \rightarrow \square'$ reversion were observed at the 3 slowest rates.

alloys show slightly different periods. This data suggests that \square may be related to composition, microstructure, impurities, homogeneity, or other factors.

Thermodynamic analysis

A thermodynamic analysis of the $\square \rightarrow \square'$ phase transformation provides insight into the 150°C hysteresis and the burst nature of the transformation. At equilibrium (T_0) the Gibbs' free energies of the \square and \square' phases are equal:

$$G_{\square} = G_{\square'} \quad (1)$$

Using the Second Law of Thermodynamics, we can write an equation for the change in G due to the transformation:

$$\Delta G_0^{\square \rightarrow \square'} = (\Delta E_{\text{chemical}} - T_0 \Delta S^{\square \rightarrow \square'} - P_{\text{atm}} \Delta V^{\square \rightarrow \square'}) = 0 \quad (2)$$

Because the transformation involves a 20% density change, it must require elastic and plastic work. Thus, the Second Law can be written as:

resistometry, and dilatometry suggest that the $\square \rightarrow \square'$ reversion occurs in a series of thermally activated bursts.

The temperature spacing between adjacent peaks in our DSC and resistivity data was measured and found to be essentially constant, regardless of heating rate. Thus, the bursts are periodic with respect to temperature in this alloy. To compare our data with burst behavior reported in the literature, distances (\square , in °C) between peaks were measured and plotted vs. peak number. The “tallest” peak was arbitrarily identified as peak “0”. Figure 4 shows data from our DSC and resistometry scans along with DSC data (Pu-0.56 wt% Ga) from Kitching [10] and dilatometry data (Pu-0.5 wt% Ga and Pu-0.6 wt% Ga) from Mitchell [4]. For the 0.6 wt% alloy, the period is fairly constant for all heating rates and characterization techniques. The other

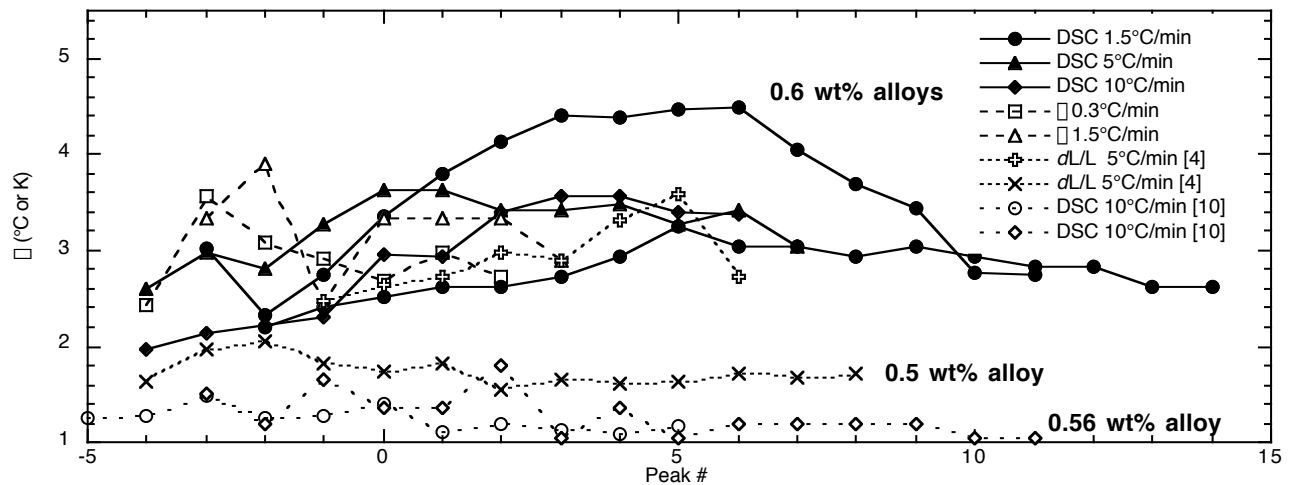


Figure 4. Periodicity of “bursts” observed with DSC (this study), resistometry (\square) (this study), dilatometry (dL/L) [4], and DSC [10].

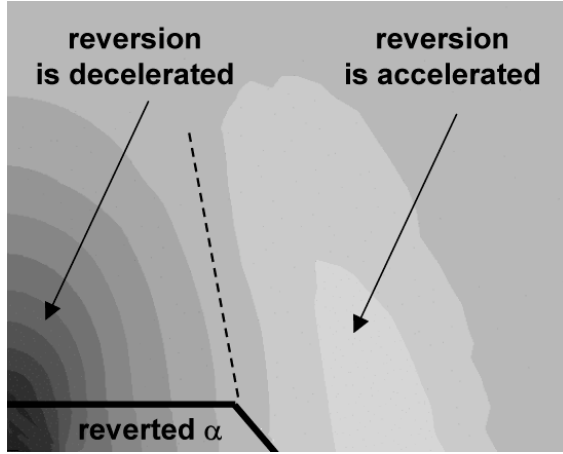


Figure 5. Finite element map of the normal stress field surrounding an α' particle which has reverted to the α -phase. The stress field accelerates reversion in front of the reverted particle and decelerates the reversion in regions perpendicular to it. The zero-stress contour is dashed.

indicated that residual stresses resulting from plastic deformation may be responsible for the spikes and steps observed with DSC, resistometry, and dilatometry. Residual stresses in the regions surrounding α' particles which have reverted back to the α phase are a result of plasticity during the transformation. Figure 5 is a finite element analysis map of the stress distribution in the region of a reverted α' particle. At the tip of the particle, the stresses aid further reversion. In regions perpendicular to the particle (along the long axis), the stresses retard further transformation. Thus, these regions may require additional heating to surmount the energy barrier for transformation. As a sample is heated during DSC, resistometry, or dilatometry, we will expect some reversion of martensite particles occurring readily at fairly low temperatures. This reversion, however, sets up a stress state that makes it difficult for further reversion. Thus, additional reversion requires more heat, and we observe another “burst” of transformation. This cycle will continue until the temperature is sufficient to revert all of the α' particles back to the α phase.

Room temperature “annealing”

Thermal cycling experiments without a prior “rest” or “hold” at room temperature do not exhibit evidence of transformation to α' on cooling. Specifically, the DSC trace does not show a peak above the background. Upon heating, however, a peak corresponding to the $\alpha' \rightarrow \alpha$ reversion provides evidence that some transformation occurred during cooling. The amount of reversion (and, hence, transformation), however, is smaller than the amount observed after a room temperature “rest.” Thus, we found that a single sample could be thermally cycled many times with the same amount of transformation during each cycle, provided that it was annealed at 375° for 8 hours, and then allowed to “rest” at room temperature for at least six hours.

To investigate this behavior further, we held samples at room temperature for various lengths of time between annealing at 375°C and the next thermal cycle. Holds ranged from 0 to 87 hours. Between each experimental run, we did a control run to verify that the sample returned to the same starting point each time. In the control runs, the room temperature hold was 12 hours. Each experimental and control run was followed by a thermal cycle. Figure 6 shows the $\alpha' \rightarrow \alpha$ reversion portion of the DSC thermal scans (note that “spikes” are not apparent in these scans because they were done at 20°C/min). The extent of the transformation is calculated from the area under the DSC peak. From Figure 6, it is clear that as the time held at room temperature decreases, the amount of transformation also decreases. It is important to note that the control runs show exceptional reproducibility, attesting to the fact that a satisfactory annealing sequence can be implemented which allows a sample to be cycled many times. It is also interesting to note

$$\Delta G_{\text{specimen}} = (\Delta E_{\text{chemical}} - T_0 \Delta S - P_{\text{atm}} \Delta V) + (\Delta E_{\text{elastic}} + \Delta Q_{\text{plastic}}) < 0 \quad (3)$$

Since the reaction occurs at atmospheric pressure and the overall volume of the sample does not change, we can obtain expressions for the width of the hysteresis:

$$M_s - T_0 = \frac{(\Delta E_{\text{elastic}} + \Delta Q_{\text{plastic}})}{\Delta S}$$

$$A_s - T_0 = \frac{(\Delta E_{\text{elastic}} + \Delta Q_{\text{plastic}})}{\Delta S}$$

where M_s and A_s are the martensite start and austenite start temperatures, respectively. The value of $\Delta E_{\text{elastic}} + \Delta Q_{\text{plastic}}$ can be calculated using finite element techniques [9].

Preliminary finite element calculations of the elastic and plastic works of transformation also

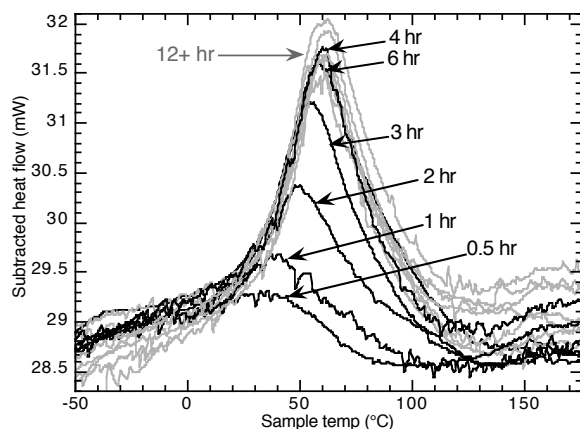


Figure 6. DSC scans (heating portions) of samples allowed to “rest” at room temperature for various lengths of time. The amount of transformation is related to the length of time the sample “rests” at room temperature, but this effect appears to saturate after about 4-6 hours.

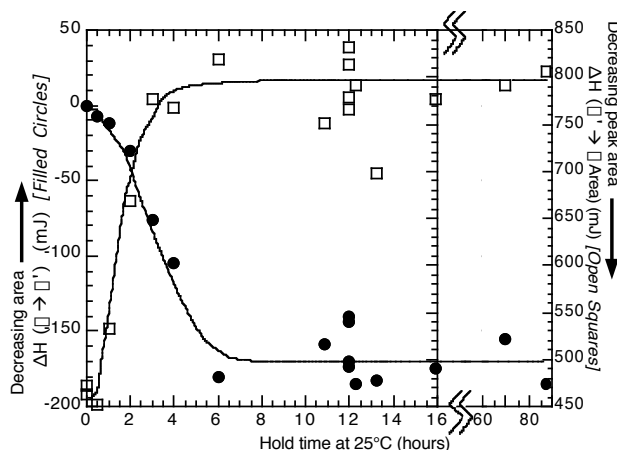


Figure 7. Measured ΔH for transformation of β' to β (left y-axis) and reversion of β' to β (right y-axis). ΔH for the reaction is the area of the DSC peak. Note that $\Delta H_{\beta' \rightarrow \beta}$ values are negative for this exothermic reaction. Thus, peak areas decrease toward the top of this y-axis. The opposite is true for the endothermic $\beta' \rightarrow \beta$ reversion.

in Figure 6 that the 4 and 6 hour hold have similar areas to the 12 hour holds. The areas of all these peaks, as well as some additional long holds, and the areas of $\beta \rightarrow \beta'$ peaks, are plotted in Figure 7. Note that the left y-axis corresponds to the exothermic $\beta \rightarrow \beta'$ transformation where the areas are negative. In this case, the amount of transformation increases as the numbers become more negative (larger absolute value). The opposite is true for the right y-axis which corresponds to the endothermic $\beta' \rightarrow \beta$ reversion. Figure 7 quantitatively indicates that the effect of the room temperature hold saturates after approximately 6 hours.

We are currently investigating why this room temperature hold is essential for transformation in a sample thermally cycled many times. At room temperature, radiation damage may accumulate in the sample [11]. This damage may provide nucleation sites for β' particles, thus enabling the transformation at low temperatures. A second possibility is that β' growth at low temperatures is dependent on the prior diffusional growth of small β nuclei at intermediate temperatures below the eutectoid of 97°C [1]. These nuclei would not grow to any significant size because of the elastic constraint of the β matrix, but they could form near defects such as grain boundaries where the elastic constraint is reduced. Formation of these nuclei is not thermodynamically possible above the eutectoid temperature and is kinetically constrained below room temperature.

CONCLUSIONS

The $\beta \rightleftharpoons \beta'$ phase transformation in a Pu-0.6 wt% Ga alloy was investigated with differential scanning calorimetry and resistometry. Martensite start and austenite start temperatures of -120°C and 35°C , respectively, were established for this alloy. DSC and resistometry data were in excellent agreement on these temperatures.

Upon heating in the DSC, “spikes” were observed during the $\beta' \rightarrow \beta$ reversion; similarly, “steps” were observed in the resistometry trace. These “steps” and “spikes” were periodic with respect to temperature. Similar behavior has been observed by other groups in DSC and dilatometry studies. For a given alloy, the period of these spikes and steps is independent of heating rate and characterization technique. No systematic variation with composition, microstructure, homogenization, impurity content, or other factors has been confirmed yet.

A single sample exhibited reproducible thermal cycling behavior as long as it was annealed at 375°C for 8 hours and then allowed to “rest” at room temperature for a minimum of 6 hours

before the next thermal cycle. During this room temperature hold, radiation damage may accumulate, providing nucleation sites for the martensitic transformation to β' on cooling. Diffusional growth of small β nuclei may also occur during the room temperature hold. This effect appeared to saturate after approximately 6 hours.

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REFERENCES

1. S. S. Hecker and L. F. Timofeeva, Los Alamos Science **26**, 244 (2000).
2. N. T. Chebotarev, E. S. Smotriskaya, M. A. Andrianov, and O. E. Kostyuk, in *Plutonium 1975 and other actinides*, edited by H. Blank and R. Lindner (North Holland Publishing Co., Amsterdam, 1975), p. 37.
3. J. T. Orme, M. E. Faiers, and B. J. Ward, in *Plutonium 1975 and other actinides*, edited by H. Blank and R. Lindner (North-Holland Publishing Company, Amsterdam, 1975), p. 761.
4. J. N. Mitchell, M. Stan, D. S. Schwartz, and C. J. Boehlert, Met. and Mat. Trans., accepted for publication (2003).
5. T. F. J. Pijpers, V. B. F. Mathot, B. Goderis, R. L. Scherrenberg, and E. W. van der Vegte, Macromolecules **35**, 3601 (2002).
6. R. B. Gibney and T. A. Sandenaw, Los Alamos National Laboratory Report No. LA-1883 (1954).
7. J. Joel, C. Roux, and M. Rapin, J. Nucl. Mater. **40**, 297 (1971).
8. S. S. Hecker, D. R. Harbur, and T. G. Zocco, Progress in Materials Science, in press.
9. C. R. Krenn, Modelling Simul. Mater. Sci. Eng., accepted for publication (2003).
10. S. Kitching, P. G. Planterose, and D. C. Gill, presented at Plutonium Futures—The Science, Albuquerque, NM, 2003 (American Institute of Physics), p. 79.
11. M. J. Fluss, B. D. Wirth, M. Wall, T. E. Felter, M. J. Caturla, A. Kubota, and T. Diaz de la Rubia, in press, J. Alloys and Compounds (2003).